California Environmental Protection Agency

Air Resources Board

Engineering and Laboratory Branch
Monitoring and Laboratory Division

SOP MLD 050

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF AMBIENT AIR OXYGENATED HYDROCARBONS (OHCs) USING SUMMA CANISTER SAMPLING AND GAS CHROMATOGRAPHIC ANALYSIS

EFFECTIVE DATE: October 1, 1997
APPROVAL DATE: March 11, 1999
REVISION NUMBER: 2.0

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State of California
Air Resources Board
Monitoring and Laboratory Division
SOP MLD 050
Standard Operating Procedure for the Determination of
Ambient Air Oxygenated Hydrocarbons (OHCS)
Using Summa Canister Sampling and
Gas Chromatographic Analysis

1 SCOPE

This document describes the sampling and analysis procedure for determination of oxygenated compounds from ambient air samples. The method was originally developed by the Engineering and Laboratory Branch (ELB), Organics Laboratory Section. Revision 2.0 of this SOP has some significant changes from the earlier version. It applies to: methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), tert-amyl methyl ether (TAME), acetone, tertiary butyl formate (TBF), and ethanol. However, only the three ethers are quantitated presently because they are either already being used or might be used as oxygen additives to the Federal and State reformulated gasolines.

2 SUMMARY OF METHOD

Ambient air is collected in SUMMA passivated stainless steel canisters using a Xontech 910A sampler. A detailed sampling procedure can be found in the MLD Quality Assurance Manual, Volume II, Appendix Q or in the U.S. EPA Method TO-14.

A 100 cc ambient air sample is drawn from the pressurized canister by a house vacuum with the aid of a mass flow controller to a cryogenic sample trap. The trap is packed with silanized glass beads and cooled to a subambient temperature (-100° C) with liquid nitrogen. A digital flow meter readout attached to the Gas Chromatograph (GC) provides a visual indication of the proper sample flow during the sampling cycle. The concentrated sample in the trap is thermally desorbed directly on to a pre-column (DB-WAX) of a multi-dimensional GC. The pre-column does the preliminary separation as well as the moisture management. At the point when all three ethers are eluting from the pre-column on to one of two analytical DB-1 columns, the column switching valve that connecting the three columns is actuated. The DB-WAX column is now in series with Column #2 where water and other late eluting compounds will be collected. The auxiliary helium supply is then connected to Column #1. The ether components eluting from Column #1 are then detected by a flame ionization detector (FID A), while other OHCs eluting from column 2 is monitored by FID B. The targeted ether peaks are identified by their characteristic retention times, and quantitated in parts per billion by volume (ppb v) by comparison to an external standard. The non-ether components are not processed at present time.

3 INTERFERENCES AND LIMITATIONS

3.1 Oxygenated compounds in the gaseous phase have long been suspected to be unstable in a compressed gas cylinder. Adding hexane and benzene to an oxygenated compound mixture enables one to monitor the stabilities of the oxygenates.

3.2 Although the analytical system may be capable of detecting other oxygen and non-oxygen containing compounds, only the three ethers, MTBE, ETBE, and TAME, are addressed by this procedure.

3.3 All compounds are identified by retention time. Compounds having similar GC retention times may co-elute, causing misidentification or inaccurate quantitation.

3.4 Variations in the SUMMA canisters, such as unevenly treated interior surfaces, leaky valves, or fittings, and humidity levels can affect the outcome of a sample or standard. MTBE has been reported stable in a humidified passivated canister for up to 31 days (Pate et al, 1992).

4 APPARATUS

4.1 A Varian Model 3600 GC system is equipped with three capillary columns (a J&W 30 m DB-WAX with 0.32 mm i.d. and 0.5 micron film thickness, and two 60 m DB-1s with 0.32 mm i.d. and 1 micron film thickness) and two flame ionization detectors (FID) with 0.01 inch flame tip. The Varian 3600 GC is modified by Lotus Consulting so that trace level hydrocarbon air samples can be concentrated and subsequently analyzed with near-full automation. The major additions to the Varian 3600 GC system are: a multi-position automated sampler with a 8134 Stream Selector Valve (SSV); a low pressure regulator (LPR) for consistent sample input pressure; three high performance valves (#2, #3, and #4) for high/low concentration sample or standard selection, and numerous other usages; a 1/8th inch nickel tubing cryotrap packed with silanized glass beads for sample trapping; a mass flow controller that is calibrated to deliver a flow from 0 to 100 cc/min for Helium with an inlet pressure of 80 psi; a column switching valve (#1); and two FIDs. FID A is used to detect signals from ether components, FID B for monitoring non-ether OHCs.

4.2 Varian GC Star Workstation, IBM PC compatible, for GC system control, automation, and method editing. **Appendix I**.

4.3 Perkin-Elmer Nelson Turbochrom Revision 4.1 or later version, IBM PC based, for data collection, storage, and integration. **Appendix II**.

4.4 Bubble flowmeter (mechanical or digital), capable of measuring accurate gas flow to 0.1 cc/min.

4.5 Stopwatch, capable of measuring 1/100 second.

4.6 Stainless steel canisters with interior surfaces treated by the SUMMA passivation process used for sample and standard storage.

4.7 The LPR must have a Teflon inner diaphragm.

4.8 The metal tubing (1/16") that connects the 16-port SSV to the sample trap and to the Teflon sample lines is made of fused silica-lined SilcoSteel; those lines are being heated to 90° C by Detector B's temperature control board. The 1/8" to 1/16" reducers from Teflon to SilcoSteel tubing are made of SilcoSteel.

5 REAGENTS

5.1 Sample blank in SUMMA canister is used for the instrument check. System blank (e.g., zero air, ultra pure air, or ultra pure nitrogen) is humidified and introduced into the system in the same manner as a sample.

5.2 National Institute of Standards and Technology (NIST), eight-component standard mix (Cyl.# AAL-053319) have been used since April 1, 1998 for both initial multipoint and daily multipoint calibrations. The certified concentration of the NIST standard mix for each component in ppb moles is:

MTBE	5.9	+/-	0.3
ETBE	5.9	+/-	0.3
TAME	4.4	+/-	0.2
Hexane	5.0	+/-	0.2
Benzene	6.0	+/-	0.2
Ethaol	26.4	+/-	1.3
Acetone	10.8	+/-	0.5
tert-Butyl formate	7.0	+/-	0.4

Scott Specialty Gases, Inc. seven-component standard mix (Cyl.# CAL010737) was used for both initial and daily multipoint calibrations before April 1, 1998. The certified concentration in ppb moles with an analytical accuracy of +/- 20% by Scott Specialty

Gases for each component is:

MTBE	12.00
ETBE	5.67
TAME	6.00
Hexane	5.91
Benzene	5.67
Ethanol	120.00
Acetone	56.5
Balanced with Nitrogen	

5.3 Scott-Marrin Inc., Cyl.# CC109953, for control standard. The reported concentration in ppb moles for each compound is:

MTBE	5.0
ETBE	5.0
TAME	5.0
tert-Butyl formate	5.0
Acetone	10
Ethanol	20
Hexane	4.8
Benzene	5.3
Balanced with Nitrogen	

5.4 NIST ALM-024324, for reference standard. The certified concentration for hexane is 5.0 ppb moles in nitrogen.

5.5 Helium, Grade 5 or equivalent, GC carrier gas.

5.6 Nitrogen, Grade 5 or equivalent, system purge and FID makeup gas; also for valve actuation.

5.7 Hydrogen, 99.99% or better, compressed or a generator such as Elhygen Mark V by Milton Roy, as a fuel for the FIDs.

5.8 Ultra zero air or purified in-house air, as an oxidant for the FIDs.

5.9 Liquid Nitrogen for cryogenic pre-concentration and sub-ambient GC analysis. A tank pressure relief of 30 psig is preferred.

5.10 Ultra-pure water, HPLC grade or equivalent, for hydrocarbon stabilization in the Summa canisters. 150 μl of water is injected to a clean, pre-evacuated canister before it is filled up to 30 psig with a standard or a blank.

6 INSTRUMENT CONFIGURATION AND PARAMETERS:

6.1 The analytical system and automation configurations in a STANDBY condition is shown in **Figure 1**.

6.2 Varian Star Workstation is used for setting the instrument parameters and to control the instrument. Several methods are developed for a routine sample analysis. They are described in Appendix I. A pre-injection program (PIP) in a sample list file is used for determining the sample volume trapped. A typical PIP for a 100 cc of sample volume is set as:

TIME (MIN)	RELAY 1	RELAY 2	RELAY 3	RELAY 4	MODE
0.00	-	-	-	-	Standby
0.01	-	-	+	-	Sample Purge
2.00	-	+	+	-	Load Trap
6.00	-	+	-	-	End Loading/N2 Flush
6.30	-	+	-	+	Isolate Trap/Start TC4
6.35	-	-	-	+	Read for GC

Return Relays to initial conditions at run end.

Typically the MFC is set at 25 cc/min, a total of 100 cc of sample is a result of 4 minute trapping time. To run a sample in the dilution mode, a smaller volume is trapped by shortening the trapping time while keeping the MFC constant.

6.3 GC Temperature Zone Settings:

ZONE	DESCRIPTION	TEMPERATURE (°C)	
Inj B	Cryotrap	-100	for Trapping
		289	for Desorption
Aux A	Valves # 2, 3, & 4	150	Isothermal
Aux B	Autosampler Valve	100	Isothermal
Det A	FID A & FID B	300	Isothermal
Det B	Samp Line, LPR	90	Isothermal

6.4 GC Gas Supply Parameters:

TYPE	CYLINDER PSI	FLOW CC/MIN	FUNCTION	SETTINGS @150° C COL. T.
Helium	100	2.5	Primary Carrier	FC 2.00
				PR 49.8
Helium	100	2.5	Auxiliary Carrier	FC 3.65
				PR 20.0
Nitrogen	80	22.5	Makeup for FID A&B	
Hydrogen	40	25	Fuel for FID A&B	
Zero Air	60	300	Oxidant for FID A&B	
Nitrogen	80	30-50	Purge Gas	FC 35.0
				PR > 60
Nitrogen	60		Valve Actuation	

Note: FID A channel is used as vent.

6.5 GC Column Temperature Program:

	1	2	3
OVEN TEMPERATURE (°C)	20	116	220
RAMP RATE (°C/min)	8	30	0
HOLD TIME (min)	10.5	0	14.04

Thermal Stabilization Time: 2.00 min

Total Run Time: 40.00 min

GC Relays Section:

TIME (MIN)	RELAY 1	RELAY 2	RELAY 3	RELAY 4	DESCRIPTION
0.00	-	-	-	-	Initial State
0.01	-	-	-	+	Sync. Delay
3.00	-	-	-	-	Inject
10.1	+	-	-	-	Column Switching

Not to return to initial state at run end.

7 PROCEDURE

7.1 Sample preconcentration

7.1.1 Varian GC Star Workstation is used for GC system configuration, sample file list, sequence list, and method building. (Reference: Varian GC Star Workstation Manual by Randall Bramston-Cook).

7.1.2 PE Nelson Turbochrom data systems are set up for data acquisition, storage, and integration (Appendix II).

7.1.3 Canister samples are connected to the autosampler using appropriate tubing and fittings. After autosampling lines are evacuated and leak-checked, the valve of the sample container can be opened. An optional line purge task can be accomplished in either manual mode or with the method PURGE18.MTH. To purge a line manually,

press and hold the button located on the left side of instrument panel which opens Valve #3, open the connected canister valve when the MFC reads 0, and advance to the next port when it reads 25. With a purge method PURGE18.MTH, Valve #3 is opened automatically by the method.

7.1.4 After sample lines are purged, activate a sample analysis method named MLD50.MTH. When all the temperature zones reach the set points and a pre-set equilibration time counts down to zero, a sequence file named MLD50.SEQ containing a sample list file named MLD50xxx.SMP and corresponding method can then be activated. A method named IDLE18.MTH should be put at the end of a sequence for storing the GC in "idle" mode.

7.1.5 The PE Turbochrom data acquisition for each sample in its sequence file (same as Star's sample list file) is started when Relay #4 is ON. Note: the Relays #2 and #4 for Valve #2 and #4 are swapped from the original manufacture's configuration so that TurboChrom data acquisition can start at the end of the cryotrap sample loading cycle.

7.2 Analysis

7.2.1 A system blank is first run to evaluate the system's cleanliness. The background level must be lower than two times the method limit of detection for each target compound.

7.2.2 The system daily four-point calibration is then performed by analyzing the NIST 8-component standard (Cyl.# ALL-053319).

7.2.3 The control standard (Scott-Marrin Cyl.# CC109953) is analyzed next, before any ambient air sample is run, in order to evaluate whether the instrument is "in-control". Results of MTBE, ETBE, and TAME are checked against their pre-established control limits.

7.2.4 Ambient air samples in SUMMA canisters are introduced by trapping 100 cc volume (Volume = 4.0 min x 25 cc/ml) of sample. After analysis, the resultant peaks are identified by retention times and quantified relative to the standard responses. A typical chromatogram of an ambient air sample is shown in **Figure 2**.

Loop analysis option of the GC system is normally not used for ambient air sample analysis, it is only designed to be used in the special auto exhaust samples and special cylinder standard analysis where concentrations are higher.

7.2.5 Duplicate analysis is performed on at least 10 percent of all ambient samples received from the field. The relative percent difference of the duplicate analysis for concentration greater than 5xLOD (Limit of Detection) is recorded and accounted in the method quality control report.

8 QUALITY CONTROL

8.1 Blank

A laboratory blank is a canister of either nitrogen or zero air that has been humidified with 150 μl of HPLC grade water. This blank must be analyzed before any standard or sample is run. The result of any single analyte in the blank must be less than two times the method detection limit in order to validate any subsequently analyzed samples. Trip blanks, whenever is available, are analyzed like samples and their results are documented and evaluated.

8.2 Multipoint Calibration

Initial multipoint analysis must be performed every year to verify precision, linearity, and method limit of detection. This is done by performing triplicate analyses of at least five simulated concentration levels of the NIST eight-component standard mix (Cyl.# AAL053319). A multipoint calibration should also be performed under the following conditions: a.) When the column is changed, b.) when major maintenance is performed, and c.) when there is a change in matrix or reagent.

Linearity, and LOD determinations are presented in **Figure 3A** , **3B**, and **3C**.

Linearity is measured as R Squared from the regression output of a plot of area count versus concentration. The R Squared value must be 0.99 or better. The LOD is obtained from the formula:

$$LOD = |\text{x-intercept}| + 3\ SD / Slope$$

SD used in this calculation is the standard deviation of the replicate analyses of the lowest standard concentration which is within 5 times the estimated LOD.

In the event where the lowest standard concentration is above 5 times the estimated detection limit, the following formula is used:

$$LOD = |\text{x-intercept}| + 3(RSD)|\text{x-intercept}|$$

where RSD is the relative standard deviation of the lowest standard analyzed.

The LODs for this method are established as:

MTBE	0.3 ppb v
ETBE	0.2 ppb v
TAME	0.2 ppb v

All subsequent multipoint calibration must be able to achieve these LODs.

8.3 Daily Calibration

Four-point calibration from the calibration standard is performed daily to establish a new set of response factors.

8.4 Control Standard

The Scott-Marrin's standard mix, Cyl.# CC109953, is chosen to be the control standard. Analysis results of MTBE, ETBE, and TAME in this standard are recorded and used to generate control charts. At least 20 data are needed for this purpose initially. Upper and lower control limits are three times the standard deviations from the average; upper and lower warning limits are two times the standard deviation of the average. Control standard must be within a preestablished control limits of 15% for sample to be valid.

8.5 Method Precision

Precision is measured in two ways, duplicate analysis and collocated analysis. The frequency of duplicate analysis is 10% of the total samples. The relative percent difference (RPD) of the ambient air sample duplicate analyses must be within the established criteria limit of 15%. The RPDs from collocated sample analyses are used to evaluate method precision including both sampling and analysis performance. Its value is estimated at 25%.

8.6 Method Accuracy

Accuracy is accomplished by analyzing other standard reference materials periodically. The results of replicate analyses of these materials must be within 20% agreement with their reported values. Audit samples, whenever available, are also analyzed and the results are used for method accuracy check.

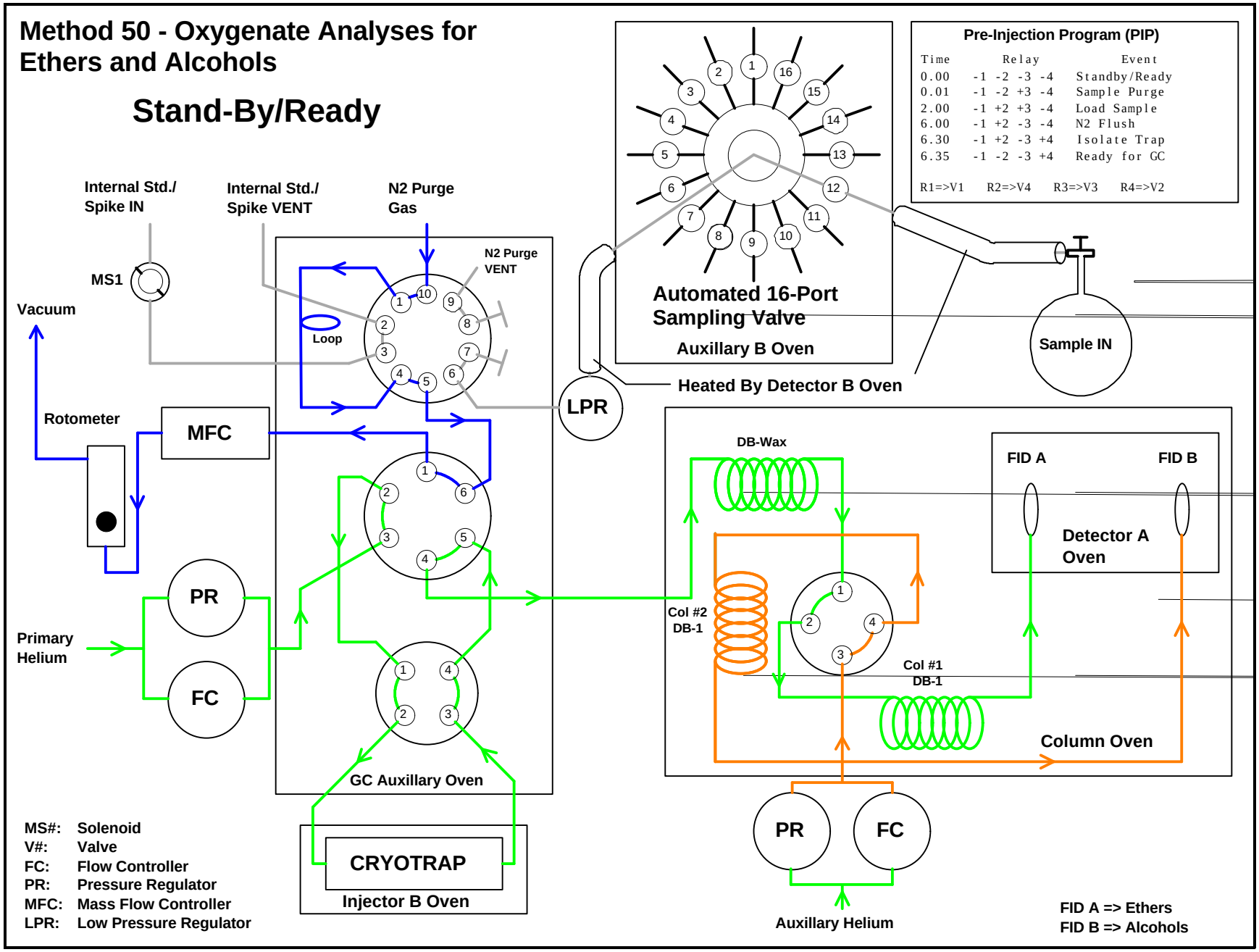


FIGURE 1: VARIAN 3600 GC SYSTEM SCHEMATICS

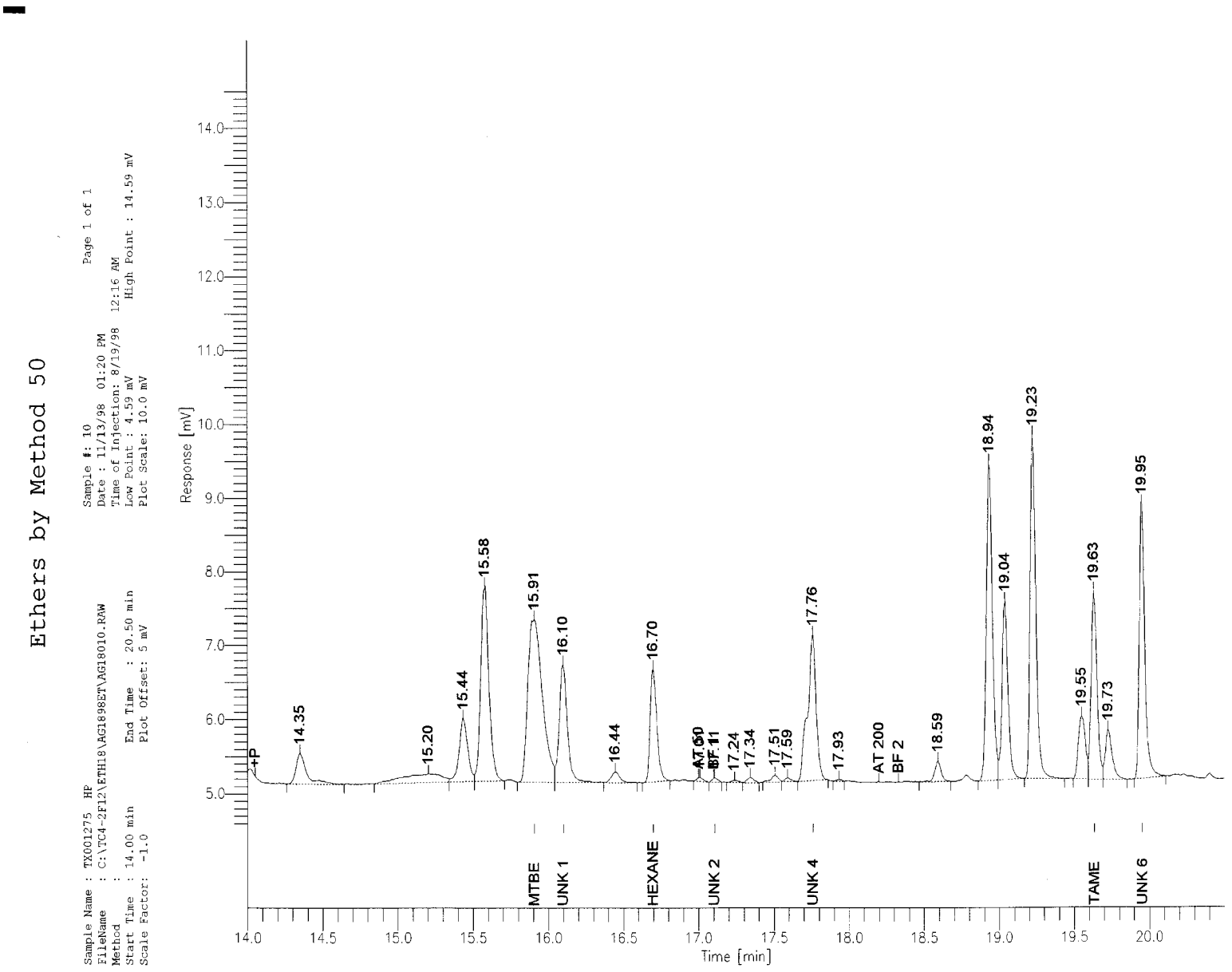


FIGURE 2. A TYPICAL AMBIENT AIR SAMPLE CHROMATOGRAM.

FIGURE 3A

Multipoint Calibration Analysis for MTBE

Calibration Date: 04/08/98 OP'S\COMPLETE\sop_50\MPCA898.WB2

Calibrated by : BC

Instrument Response (Area Counts = ac)

ppb =>	0.74	2.95	4.43	5.90	8.85	10.33	11.80
Area (ac)	ac	ac	ac	ac	ac	ac	ac
Run #							
1	2494	10648	16003	21511	32343	38136	43613
2	2407	10252	16110	21512	32106	37643	43774
3	2315	10579	15770	21480	32228	38244	43680
4	2331						
5	2257						
6	2162						
7	2232						
8	2172						
Mean (ac) =	2296	10493	15961	21501	32226	38008	43689
Std.Dev (ac)	114.68	211.54	173.85	18.19	118.52	320.39	80.88
% RSD =	4.994	2.016	1.089	0.085	0.368	0.843	0.185
# Obs. =	8	3	3	3	3	3	3

X-Conc.	Y-Area	Predicted Y
	Mean Response	Predicted Response
0.74	2296	2228.080
2.95	10493	10474.068
4.43	15961	15996.267
5.90	21501	21481.155
8.85	32226	32488.242
10.33	38008	38010.442
11.80	43689	43495.329

Regression Output:

Constant		-533.02
Std Err of Y Est		150.40
R Squared		0.99992
No. of Observations		7
Degrees of Freedom		5
Degrees of Freedom		
X Coefficient(s)	3731.22	
Std Err of Coef.	15.14	

LOD Calculations:

X-Intercept [-(b/a)]	=	***0.143***	ppb
Std. Dev. of Response at Lowest Level	=	114.679	ac
Slope of the Regression Line	=	3731.216	ac/ppb
3 * (Std. Dev.)/(Slope)	=	***0.092***	ppb
LOD Estimate	=	| X-Intercept | + 3(Std. Dev./Slope)	
	=	**0.235**	**ppb**

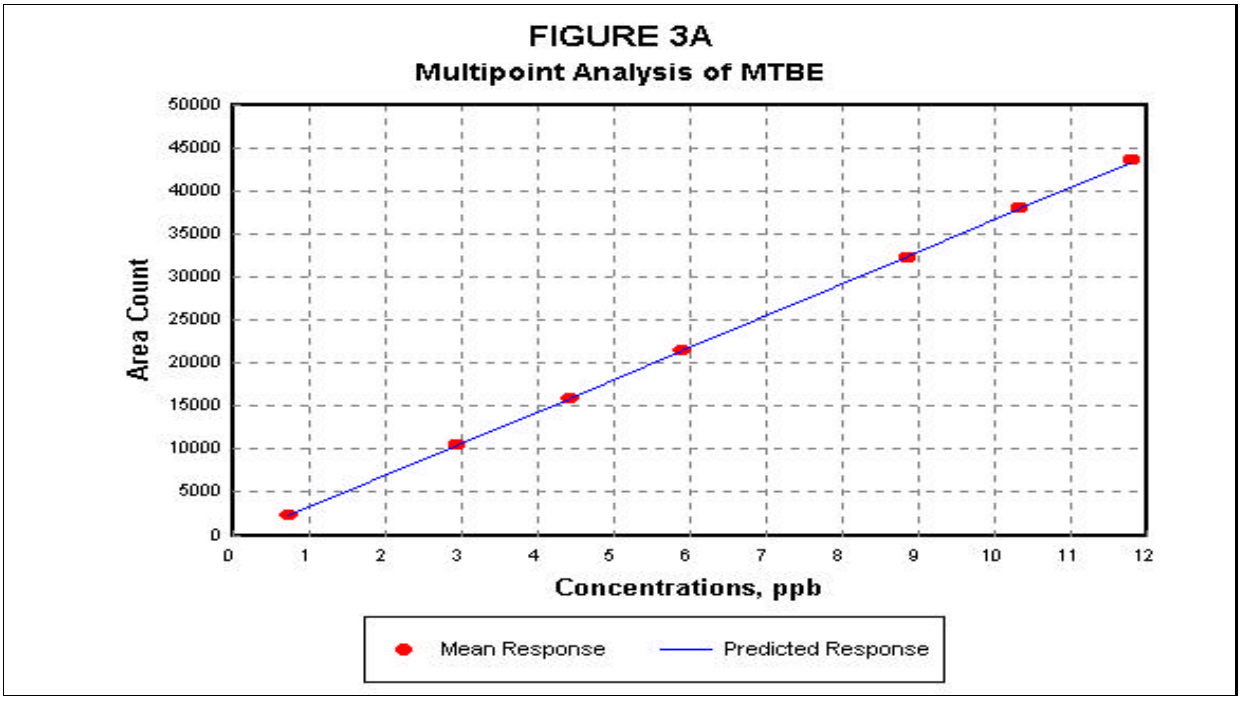


FIGURE 3B

Multipoint Calibration Analysis for ETBE

Calibration Date: 04/08/98 A:\MPCA898.WB2
Calibrated by : BC
Instrument Response (Area Counts = ac)

ppb =>	0.74	2.95	4.43	5.90	8.85	10.33	11.80
Area (ac)	ac	ac	ac	ac	ac	ac	ac
Run #							
1	2524	12160	18579	25202	37494	43974	51083
2	2641	12170	18296	24833	37988	44108	50883
3	2702	12006	18386	24954	38163	44298	51422
4	2490						
5	2711						
6	2618						
7	2582						
8	2672						
Mean (ac) =	2618	12112	18420	24996	37882	44127	51129
Std.Dev (ac	80.77	91.93	144.59	188.11	346.94	162.80	272.47
% RSD =	3.086	0.759	0.785	0.753	0.916	0.369	0.533
# Obs. =	8	3	3	3	3	3	3

X-Conc.	Y-Area	Predicted Y
	Mean Response	Predicted Response
0.74	2618	2450.920
2.95	12112	12114.947
4.43	18420	18586.784
5.90	24996	25014.892
8.85	37882	37914.836
10.33	44127	44386.673
11.80	51129	50814.781

Regression Output:

Constant		-785.00
Std Err of Y Est		211.40
R Squared		0.99988
No. of Observations		7
Degrees of Freedom		5
Degrees of Freedom		
X Coefficient(s)	4372.86	
Std Err of Coef.	21.28	

LOD Calculations:

X-Intercept [-(b/a)]	=	***0.180*** ppb
Std. Dev. of Response at Lowest Level	=	80.768 ac
Slope of the Regression Line	=	4372.863 ac/ppb
3 * (Std. Dev.)/(Slope)	=	***0.055*** ppb
LOD Estimate	=	| X-Intercept | + 3(Std. Dev./Slope)
	=	**0.235 ppb**

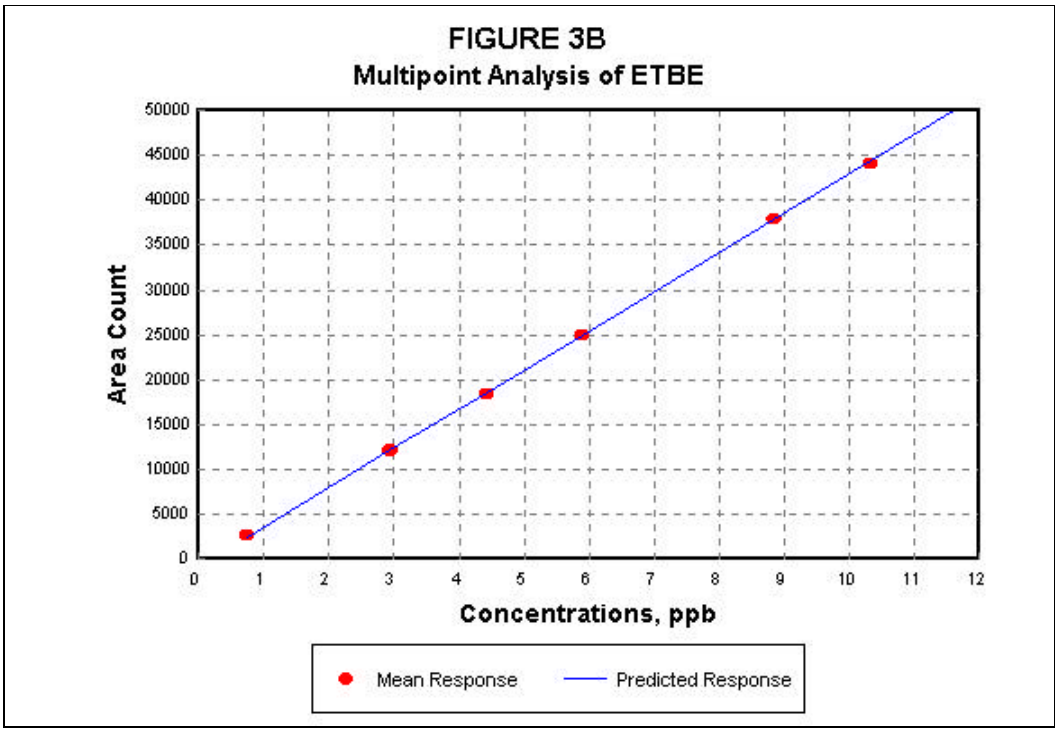


FIGURE 3C

Multipoint Calibration Analysis for TAME

Calibration Date: 04/08/98 A:\MPCA898.WB2

Calibrated by : BC

Instrument Response (Area Counts = ac)

ppb =>	0.55	2.20	3.30	4.40	6.60	7.70	8.80
Area (ac)	ac	ac	ac	ac	ac	ac	ac
Run #							
1	1830	8668	13134	17475	26684	30396	35700
2	1952	8701	13286	17982	26397	31630	35358
3	1927	8786	13384	17950	27115	31556	
4	1912						
5	1922						
6	2064						
7	1883						
8	1951						
Mean (ac) =	1930	8718	13268	17802	26732	31194	35529
Std.Dev (ac	67.07	60.88	125.97	283.93	361.40	692.08	241.83
% RSD =	3.475	0.698	0.949	1.595	1.352	2.219	0.681
# Obs. =	8	3	3	3	3	3	2

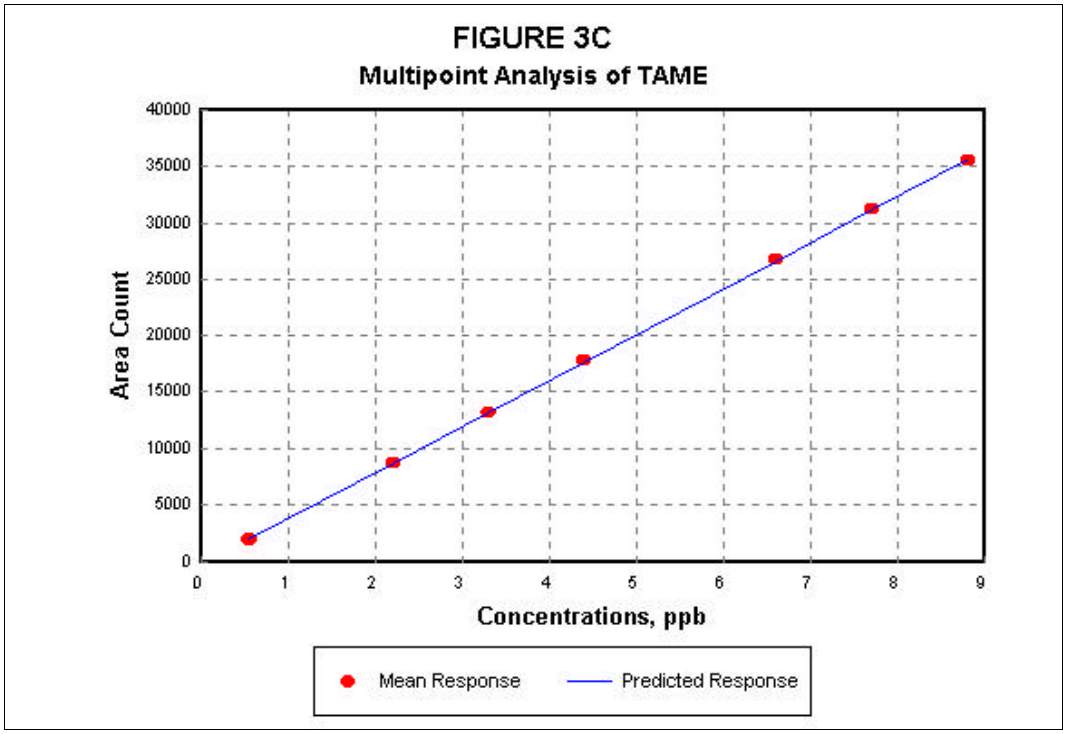
X-Conc.	Y-Area	Predicted Y
	Mean Response	Predicted Response
0.55	1930	2011.362
2.20	8718	8738.821
3.30	13268	13223.793
4.40	17802	17708.766
6.60	26732	26678.711
7.70	31194	31163.683
8.80	35529	35648.656

Regression Output:

Constant		-231.12
Std Err of Y Est		84.62
R Squared		0.99996
No. of Observations		7
Degrees of Freedom		5
Degrees of Freedom		
X Coefficient(s)	4077.25	
Std Err of Coef.	11.42	

LOD Calculations:

X-Intercept [-(b/a)]	=	***0.057***	ppb
Std. Dev. of Response at Lowest Level	=	67.068	ac
Slope of the Regression Line	=	4077.248	ac/ppb
3 * (Std. Dev.)/(Slope)	=	***0.049***	ppb
LOD Estimate	=	| X-Intercept | + 3(Std. Dev./Slope)	
	=	**0.106 ppb**	



APPENDIX I

VARIAN GC STAR WORKSTATION

The Varian GC Star Workstation operates under MS-DOS and uses Microsoft Windows 3.1 or later version. The Workstation controls the instruments, automates data collection and analysis, and documents the results of a chromatographic run. For a general application of the Star Workstation software, please refer to the Star Chromatography Workstation Operational Manual, Varian Chromatography Systems (1993), Varian GC Star Workstation Manual and Ultra-Trace Hydrocarbon System Operator's Manual by Randall Bramston-Cook.

The Star Workstation is capable of data handling and reporting. However, PE Nelson Trubochrom software is chosen for several reasons: familiarity, smaller data files, and ease in transfering to LIMS. The Star files are recorded also for the purpose of monitoring the instrument condition and backing up Turchrom data files.

Several methods are normally programmed for each instrument in its associated Star Workstation. Each instrument has a configured address in the Analog-to-Digital Converter Board (ADCB), installed in an IBM compatible PC. Each ADCB is capable of handling up to four instruments. A bus address of a GC (Instrument Control / Auto Control Module Box) needs also to be configured and its address number is one number greater than its ADCB's. As an example, for an instrument named MTBE-18, ADCB is addressed at 18 and GC Control is at 19. A method named MLD50 for sample analysis is attached to this instrument. Other methods used for System MTBE-18 includes IDLE18.MTH for system standby, BAKE18.MTH for conditioning (bakeout) the system, and PURGE18.MTH for autosampler line purging are necessary and/or helpful in the process of routine analysis and maintenance. Since Star Workstation is not used for data handling and reporting, the sample method MLD50.MTH does not include these sections.

STAR METHOD MLD50.MTH FOR MTBE-18.

****
Star Chromatography Workstation - Method Listing Tue Oct 13 14:07:37 1998
****

ADC Board
****
Module Address: 18

End Time : 40.00 minutes
Autozero at Start : Yes
Channel A Name : ETHERS
Channel B Name : ALCOHOLS
Channel A Full Scale : FID A
Channel B Full Scale : FID B

Detector Information
Detector Bunch Rate : 16 points (2.5 Hz)
Monitor Length : 128 bunched points (51.2 seconds)
Data File Name : star
Number Files From : 1

Integration Parameters Address 18 Channel A
Subtract Blank Baseline : No
Initial S/N Ratio : 15
Initial Peak Width : 8 sec
Initial Tangent Height % : 10%
Monitor Noise : Before every run
Measurement Type : Peak Area
Initial Peak Reject Value : 200 counts
Report Unitdentified Peaks : Yes
Normalize Results : No

Calibration Setup Address 18 Channel A
Calculation Type : External Standard
Number of Calibration Levels : 1
Curve Origin : Force
Curve Fit : Linear
Weighted Regression : (none)
Replicate Treatment : Keep Replicates Separate
Replicate Tolerance : Always add new replicates
Out -of-Tolerance Action : Increment Error Count
Calibration Range Tolerance : 100.0%
Out-of-Tolerance Action : Increment Error Count

STAR METHOD MLD50.MTH FOR MTBE-18 (CONT.)

Verification Setup Address 18 Channel A
Deviation Tolerance : 10.0%
Out-of-Tolerance Action : Increment Error Count

Peak Table Address 18 Channel A
Reference Peaks Time Windows : Width : 0.05 min. Retention Time 0.5%
Other Peaks Time Windows : Width : 0.05 min. Retention Time 0.5%
Peak Table Empty

Time Events Table Address 18 Channel A
Inhibit Integrate : 20.5000 until 40.0000

Report Format : Module ADCB Address 18 Channel A
Title : Ethers by Method 50 - FID A - Ethers
Print Chromatogram : No

Print Results : No
Convert Results to ASCII? : Off

Calibration Block Reports
Print Report : No

Converter Report to ASCII? : Off

Print Copies : 1

Intigration Parameters Address 18 Channel B

Subtract Blank Baseline : No
Initial S/N Ratio : 5
Initial Peak Width : 16 sec
Initial Tangent Height% : 10%
Monitor Noise : Before every run
Measurement Type : Peak Area
Initial Peak Reject Value : 200 counts
Report Unidentified Peaks : Yes
Report Missing Peaks : Yes

Calibration Setup Address 18 Channel B

Calculation Type : % (No Calibration)
Number of Calibration Levels : 1
Curve Origin : Force
Curve Fit : Linear
Weighted Regression : (None)

STAR METHOD MLD50.MTH FOR MTBE-18 (CONT.)

Replicate Treatment : Keep Replicates Separate
Replicate Tolerance : Always add new replicates
Out-of-Tolerance Action : Increment Error Count
Calibration Range Tolerance : 10%
Out-of-Tolerance Action : Increment Error Count

Verification Setup Address 18 Channel B

Deviation Tolerance : 10%
Out-of-Tolerance Action : Increment Error Counts

Peak Table Address 18 Channel B

Reference Peaks Time Windows : Width: 0.10 min. Retention Time 2.0%
Other Peaks Time Windows : Width: 0.10 min. Retention Time 2.0%

Peak Table Empty

Time Events Table Address 18 Channel B

Inhibit Integrate : 22.5000 until 40.0000

Report Format : Module ADCB Address 18 Channel B

Title : Alcohols by Method 50 - FIB B - Alcohols
Print Chromatogram : No

Print Results : No
Convert Results to ASCII : Off

Calibration Block Reports
Print Report : No
Convert Report to ASCII : Off

Print Copies : 1

STAR METHOD MLD50.MTH FOR MTBE-18 (CONT.)

****
3600 GC
****
Module Address : 19

GC Injector A

Injector Type	:	Not used
GC Injector Oven on?	:	No

GC Injector B

Injector Type	:	Temperature Programmable
GC Injector Oven On?	:	Yes
Initial GC Injector Temperature	:	-5 degrees C
Initial GC Injector Hold Time	:	0.50 minutes

GC Injector Temperature Program 1

Final Temperature	:	289 degrees C
Rate	:	300.0 degrees C / minute
Hold Time	:	38.52 minutes

Coolant To Injector/Aux Valve On?	:	Yes
Coolant Timeout	:	60.00 minutes

GC Auxiliary

Injector Type	:	Isothermal
GC Auxiliary Oven On?	:	Yes
GC Auxiliary Description	:	V2, V4, V3
Initial GC Auxiliary Temperature	:	150 degrees C
Initial GC Auxiliary Hold Time	:	0.00 minutes

GC Column

Column Oven On?	:	Yes
Initial Column Temperature	:	20 degrees C
Initial Column Hold Time	:	10.50 minutes
Thermal Stabilization Time	:	2.00 minutes

Coolant To Column Valve On?	:	Yes
Coolant Timeout	:	60.00 minutes

STAR METHOD MLD50.MTH FOR MTBE-18 (CONT.)

GC Column Temperature Program 1

Final Temperature	:	116 degrees C
Rate	:	8.0 degrees C / minute
Hold Time	:	0.00 minutes

GC Column Temperature Program 2

Final Temperature	:	220 degrees C
Rate	:	30.0 degrees C / minutes
Hold Time	:	14.04 minutes

GC Column A Parameters

Installed?	:	Yes
Length	:	90.0 meters
Diameter	:	320 microns
Carrier Gas	:	Helium

GC Column B Parameters

Installed?	:	Yes
Length	:	60.0 meters
Diameter	:	320 microns
Carrier Gas	:	Helium

GC Detector Heater A

Detector Heater On?	:	Yes
Detector Temperature	:	300 degrees C

GC Detector Heater B

Detector Heater On?	:	Yes
Detector Temperature	:	90 degrees C

GC Detector A

Detector Type	:	FID
Detector On?	:	Yes
Attenuation	:	8
Detector Range	:	12
Autozero at GC Ready?	:	Yes

GC Detector B

Detector Type	:	FID
Detector On?	:	Yes
Attenuation	:	8

STAR METHOD MLD50.MTH FOR MTBE-18 (CONT.)

Detector Range : 12
Autozero at GC Ready? : Yes

Autosampler

Autosampler Type : 8134 SSV

GC Relays

Relay Time Program : Use
Initial Relay States : _ _ _ _
Relay Initial Conditions at Run End? : No

GC Relay Program 1

Relay Time : 0.01 State - - - 4

GC Relay Program 2

Relay Time : 3.00 State - - - -

GC Relay Program 3

Relay Time : 10.10 State 1- - -

GC Stripchart

Stripchart On? : No

GC Col. Std by : 150°

1 : FC 2.00

2 : PR 49.8

N_2 purge : FC 35.0
: PR > 60 psi

MFC : set @ 28.8 read 30.0 25 mL/min measured with a flow meter

MU Gas N_2 : 80.0 psi

Carrier He : 100 psi

STAR METHOD MLD50.MTH FOR MTBE-18 (CONT.)

Valve N_2 : 60 psi

LPR to Port 1 : 15 psi
(N_2 from valve gas)

Cal std_{oxst} : 053319

Cont. : Cl09953

Extra Cont : 0923

APPENDIX II

PERKIN-ELMER NELSON TURBOCHROM DATA SYSTEM

DATA SYSTEM:

The PE Nelson Turbochrom version 4.1 is a software operated within the Microsoft Windows operating environment. For general application of the Turbochrom software, please refer to the Turbochrom User's Guide, Perkin-Elmer PE Nelson Division. The Turbochrom set-up information for Instrument MTBE-18 is presented below:

Method	:	MLD50.MTH
Sequence File Name	:	MLD50xxx.SEQ (i.e., MLD50f20.seq for Feb.20 sequence)
Interface Number	:	0
Channel	:	1 : FID A (ethers)
Channel	:	2 : FID B (non-ether OHCs)

The method MLD50.MET is attached at the end of this Appendix.

BASE NAME:

The Turbochrom system uses 4 characters to form the file base name. A three-digit cycle number is appended to the selected base name and the data files are stored in a specified directory. The same base name is used for storing raw, result, baseline, and modified raw files, but the three character extension differentiates one file from another. If a duplicate file name exists the system will rename the current sample. This can and will cause problems with LIMS transfer procedures. To prevent this and to allow easy identification of data, the following naming convention is used:

1. Use only a 4 character base name for data runs.
2. The first two characters will be a month code.
3. The third and fourth characters will be a date code.
4. The fifth through seventh character is automatically assigned by the Nelson system and represents the sample number for the base name.

MONTH CODES:

JAN	=	JA	JUL	=	JL
FEB	=	FB	AUG	=	AG
MAR	=	MR	SEP	=	SE
APR	=	AP	OCT	=	OC
MAY	=	MY	NOV	=	NV
JUN	=	JN	DEC	=	DC

EXAMPLE:
FB01020 WOULD BE FEBRUARY 1ST, RUN #20.

SAMPLE NAME FORMAT:

Within a sequence or during a manual download a sample name this must be entered. The sample name must be uniquely formated for LIMS to recognize.

Generally a system blank or sample of Grade 5 Nitrogen or equivalent is run as the first sample of the day to insure that the system is free of contamination.

Enter a system blank as: **Zeor Air**

After the system blank, the 4-point calibration standards are run.

Enter a Calibration standard as: **XXST53319 or OXST53319**

After the calibration standards, a control sample is run.

Enter a control sample as: **C109953**

An ambient air sample is first assigned an 8-character bar code number. Then it is logged in to SQL*LIMS to receive a 9-digit LIMS number that starts with a 2. The sample name uses the bar code number plus other relevent site information. The bar code number usually begins with TX followed by 6 digits. A space is used to separate the bar code section used for LIMS and the site information. A typical sample name would be entered as:

TX001259 MX

In the event of replicate analyses, an aphabete is added to the end of the bar code number, A-J represents the 2nd through 10th replicates. The duplicate for the above sample would be entered as:

TX001259A MX

REFERENCES:

Perkin-Elmer Nelson Turbochrom 4 Series Chromatography Data System User's Manual, 1995.

TURBOCHROM METHOD MLD50.

****

Turbochrom Method File : C:\TC4-2F12\ETH18\MLD50A.MTH <Modified>
Created by : SCM on : 11/10/97 11:22 AM
Edited by : BC on : 10/22/98 03:45 PM
Description : Ethers by Method 50 - Quantitation by 4 Level Liner Fitted Curve

Number of Times Edited : 46
Number of Times Calibrated : 780

****

Instrument Conditions :
Ethers Method 50 - Instrument MTBE-18 - FID A

Instrument Control Method :
Instrument name : MTBE_-_18

Interface Parameters :
Delay Time : 0.00 min.
Run Time : 38.00 min.
Sampling Rate : 2.0000 pts/s
Interface Type : 900
Analog Voltage Input : 1000 mV
Data will be collected from both channels

Timed Events:
There are no timed events in the method

Real Time Plot Parameters :

Channel A -- Pages	:	1	Offset	:	3.500 mV	Scale	: 10.000 mV
Channel B -- Pages	:	1	Offset	:	3.500 mV	Scale	: 8.000 mV

Processing Parameters :
Bunch Factor : 2 points
Noise Threshold : 4 μV
Area Threshold : 200.00 μV

Peak Separation Criteria
Width Ratio : 0.200
Valley-to-Peak Ratio : 0.010

Exponential Skim Criteria
Peak Height Ratio : 5.000
Adjusted Height Ratio : 4.000
Valley Height Ratio : 3.000

TURBOCHROM METHOD MLD50 (CONT.)

Baseline Timed Events :

Event #1 -	- P	at	0.020
Event #2 -	+P	at	14.050
Event #3 -	AT 50.000	at	17.000
Event #4 -	BF 1.000	at	17.100
Event #5 -	AT 200.000	at	18.200
Event #6 -	BF 2.000	at	18.330
Event #7 -	- P	at	20.550
Event #8 -	AT 200.000	at	20.855

Annotated Replot Parameters :

Offset will be autozeroed

Plot Scale	:	10.000 mV
Number of Pages	:	1
Plot Title	:	Ethers by Method 50
X-Axis Label	:	Time [min]
Y-Axis Label	:	Response [mV]
Orientation	:	Landscape
Retention Labels	:	Peak Crests
Component Labels	:	Actual Time
Start Time	:	14.00
End Time	:	20.50

Report Format files :

No report format files given

User Programs :

No user programs will be executed

Global Information :

Default Sample Volume	:	100.000 ml
Quantitation Units	:	ppb
Void Time	:	0.000 min
Correct amounts during calibration	:	YES
Reject outliers during calibration	:	NO

An External Standard calibration will be used

Unknown peaks will be quantitated using a response factor of 1.000000e+07

Component Information :

MTBE

Component Type	:	Single Peak Component			
Retention Time	:	15.849 min	Search Window	:	0.05 s, 0.50 %
Reference Component	:	HEXANE			

Find peak closest to expected RT in window

TURBOCHROM METHOD MLD50 (CONT.)

Calibrating Area versus Amount using a 1st Order Fit
Curve will ignore the origin
Amounts will not be scaled prior to the regression
Weighting factor for the regression: None

User Values:
Label :
Value 1 : 0.000000
Value 2 : 0.000000
Value 3 : 0.000000
Value 4 : 0.000000
Value 5 : 0.000000

Calibration Levels:

Level Name	Amount	Area	Height	# Replicates
1	0.7400	2205.50	448.23	1
2	2.9500	10532.00	2026.76	1
3	5.9000	22079.00	3337.19	1
4	11.8000	41646.00	5306.39	1

Calibration Curve : y = (65.926630) + (3562.355936)x
R-squared : 0.998349

Unk 1
Component Type : Single Peak Component
Retention Time : 16.063 min Search Window : 0.05 s, 0.50 %
Reference Component : HEXANE
Find peak closest to expected RT in window
Use Average Calibration Factor (Area / Amount)

User Values:
Label :
Value 1 : 0.000000
Value 2 : 0.000000
Value 3 : 0.000000
Value 4 : 0.000000
Value 5 : 0.000000

TURBOCHROM METHOD MLD50 (CONT.)

Calibration Levels :

Level Name	Amount	Area	Height	# Replicates
6	0.0001	3303.36	879.63	1

Average Calibration Factor = 3.303361e+07 (%RSD = 0.00)

HEXANE

Component Type : Single Peak Component
Retention Time : 16.667 min Search Window : 0.50 s, 1.00 %
Reference Component :
Find peak closest to expected RT in window
Calibrating Area versus Amount using a 1st Order Fit
Curve will ignore the origin
Amounts will not be scaled prior to the regression
Weighting factor for the regression : None

User Values:
Label :
Value 1 : 0.000000
Value 2 : 0.000000
Value 3 : 0.000000
Value 4 : 0.000000
Value 5 : 0.000000

Calibration Levels :

Level Name	Amount	Area	Height	# Replicates
1	0.6250	3541.00	1052.71	1
2	2.5000	16325.75	5026.61	1
3	5.0000	33733.50	10186.35	1
4	10.0000	75549.50	24395.71	1

Calibration Curve : y = (-2670.907791) + (7714.945168)x
R-squared : 0.997335

Unk 2

Component Type : Single Peak Component
Retention Time : 17.076 min Search Window : 0.05 s, 0.50 %
Reference Component : HEXANE
Find peak closest to expected RT in window
Use Average Calibration Factor (Area / Amount)

TURBOCHROM METHOD MLD50 (CONT.)

User Values:

Label :
Value 1 : 0.000000
Value 2 : 0.000000
Value 3 : 0.000000
Value 4 : 0.000000
Value 5 : 0.000000

Calibration Levels :

Level Name	Amount	Area	Height	# Replicates
6	0.0001	74.00	29.09	1

Average Calibration Factor = 740000.000000 (%RSD = 0.00)

ETBE

Component Type : Single Peak Component
Retention Time : 17.610 min Search Window: 0.05 s, 0.20 %
Reference Component : HEXANE
Find peak closest to expected RT in window
Calibrating Area versus Amount using a 1st Order Fit
Curve will ignore the origin
Amounts will not be scaled prior to the regression
Weighting factor for the regression: None

User Values :
Label :
Value 1 : 0.000000
Value 2 : 0.000000
Value 3 : 0.000000
Value 4 : 0.000000
Value 5 : 0.000000

Calibration Levels:

Level Name	Amount	Area	Height	# Replicates
1	0.7400	2488.50	645.41	1
2	2.9500	12274.00	3254.37	1
3	5.9000	25408.75	6025.68	1
4	11.8000	50713.75	9999.26	1

Calibration Curve : y = (-585.910697) + (4358.515324)x
R-squared : 0.999910

TURBOCHROM METHOD MLD50 (CONT.)

Unk 4

Component Type : Single Peak Component
Retention Time : 17.727 min Search Window: 0.05 s, 0.50 %
Reference Component : HEXANE
Find peak closest to expected RT in window
Use Average Calibration Factor (Area / Amount)

User Values :
Label :
Value 1 : 0.000000
Value 2 : 0.000000
Value 3 : 0.000000
Value 4 : 0.000000
Value 5 : 0.000000

Calibration Levels:

Level Name	Amount	Area	Height	# Replicates
6	0.0001	4599.50	1039.12	1

Average Calibration Factor = 4.599500e + 07 (%RSD = 0.00)

TAME

Component Type : Single Peak Component
Retention Time : 19.617 min Search Window: 0.15 s, 0.50 %
Reference Component : HEXANE
Find largest peak in window
Calibrating Area versus Amount using a 1st Order Fit
Curve will ignore the origin
Amounts will not be scaled prior to the regression
Weighting factor for the regression: None

User Values:
Label :
Value 1 : 0.000000
Value 2 : 0.000000
Value 3 : 0.000000
Value 4 : 0.000000
Value 5 : 0.000000

TURBOCHROM METHOD MLD50 (CONT.)

Calibration Levels:

Level Name	Amount	Area	Height	# Replicates
1	0.5500	1757.00	428.38	1
2	2.2000	8551.25	2278.78	1
3	4.4000	18005.00	4535.85	1
4	8.8000	33902.75	7960.93	1

Calibration Curve : y = (31.278107) + (3892.845616)x
R-squared : 0.998218

Unk 5
Component Type : Single Peak Component
Retention Time : 19.629 min Search Window: 0.00 s, 0.00 %
Reference Component : HEXANE
Find peak closest to expected RT in window
Use Average Calibration Factor (Area / Amount)

User Values:
Label :
Value 1 : 0.000000
Value 2 : 0.000000
Value 3 : 0.000000
Value 4 : 0.000000
Value 5 : 0.000000

Calibration Levels:

Level Name	Amount	Area	Height	# Replicates
6	0.0001	2566.50	997.60	1

Average Calibration Factor = 6.122500e + 06 (%RSD = 0.00)

Unk 6
Component Type : Single Peak Component
Retention Time : 19.940 min Search Window: 0.05 s, 0.50 %
Reference Component : HEXANE
Find peak closest to expected RT in window

TURBOCHROM METHOD MLD50 (CONT.)

Use Average Calibration Factor (Area / Amount)

User Values:

Label	:	
Value 1	:	0.000000
Value 2	:	0.000000
Value 3	:	0.000000
Value 4	:	0.000000
Value 5	:	0.000000

Calibration Levels:

Level Name	Amount	Area	Height	# Replicates
6	0.0001	2566.50	997.60	1

Average Calibration Factor = 2.566500e + 07 (%RSD = 0.00)